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Heat transfer fluid life time analysis of diphenyl oxide/biphenyl grades for concentrated solar power plants

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Abstract

To gain a better understanding of how purity affects fluid degradation in concentrated solar power (CSP) plants, commercially available eutectic diphenyl oxide/ biphenyl heat transfer fluids were tested for their thermal stability at different temperatures and for their chlorine content. A model for thermal degradation of the eutectic diphenyl oxide/ biphenyl fluids in a parabolic trough CSP plant was built based on laboratory testing results and average fluid analysis results from operating CSP plants. Fluid degradation was compared between high quality product at 99.9% purity such as DOWTHERM™ A Heat Transfer Fluid and commercially available products with purities around 99.5%. A range of 1.7-2.4 times more degradation was determined for 99.5% purity fluids compared to the 99.9% quality for the operating conditions in a CSP plant. More frequent degradation separation operations are needed for lower 99.5% purity fluids, which ultimately means extra operating cost. In addition to that, the additional new fluid refills needed over a 25 years of operation is $2/kg.

DOWTHERM™ is a trademark of The Dow Chemical Company.

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Keywords: Heat transfer fluids; diphenyl oxide; biphenyl; degradation; purity; chlorine

1. Introduction

A synthetic organic heat transfer fluid (HTF) consisting of 73.5% diphenyl oxide (DPO) and 26.5% Biphenyl is used by today's parabolic trough concentrated solar power (CSP) technology to transfer the heat from the solar collectors to the power cycle. The most commonly used grades of HTF in CSP plants have a purity as high as 99.9% and chlorine levels below the detection limit of 0.2 parts per million (ppm) and have been successfully used for over

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20 years. This grade contains high purity DPO with the lowest impurity level which is usually produced by the reaction of phenol over a catalyst. This process does not involve any chlorinated organic compounds. High quality material produced by this process will typically have non-detectable levels of chlorine since none is used in this production process.

A second method to produce DPO involves the reaction of monochlorobenzene with phenol. In this process, it is common to have some residual chlorine containing compounds left in the finished product. In reviewing producer specifications, chlorine levels of 40 ppm or even higher have been allowed in some DPO grades. These residual chlorine containing compounds can break down at elevated temperatures and result in chloride being present in the system. The reaction of the second method is also less selective, which requires a more complex separation process and leads to higher impurity concentrations such as 0.5%.

As grades with lower purity may bring advantages in regards of lower HTF cost, the effects of these alternative grades have been investigated and are discussed in this report. The most relevant HTF property is the degradation of the HTF which causes a change in the fluid properties that mostly have a negative impact to the system resulting in higher operating costs. Degradation is a chemical change of the HTF's molecules caused by many factors such as heat, oxygen, impurities and many more.

This report discusses the impact of the purity of different DPO/biphenyl grades on parabolic trough based CSP plants. The degradation behavior of other purity grades was tested [1, 2] in the past, but the meaning for the complex operation of a parabolic trough solar CSP plant has not been studied.

Laboratory test data for different DPO/biphenyl grades and sample analysis data from CSP plants were used to build a fluid life time model.

Additionally, the effects of chloride contaminants in DPO/biphenyl blends on carbon steel and stainless steel is discussed in relation to pitting corrosion and chloride stress corrosion cracking at high temperature.

2. Assumptions and analysis

2.1. Degradation testing

Thermal degradation is impacted by many factors that have been studied in diverse DOW internal reports and DOW customer feedback:

- Fluid temperature
- Initial impurity concentration (organic and inorganic)
- Concentration of degradation products in HTF
- Low boiler / high boiler ratio in the HTF
- Degradation product composition
- Oxygen accessed to the fluid (e.g. lack of Nitrogen quality)
- Metal surface to HTF mass ratio due to catalytic effects from construction materials
- Contamination of HTF (e.g. pipe conservation oil, residues from construction, oil from pump seal system, etc.)

The first three points from the above list have been covered in this study. Unused DOWTHERM™ A HTF (99.9% purity) and 5 commercially available samples of DPO/biphenyl fluids at 99.5% purity were degraded at 400°C. The degradation concentration of the samples was determined after 6 weeks. Then further degradation testing at different time periods of heat exposure at 371°C, 399°C and 427°C were performed for unused DOWTHERM™ A HTF and one representative grade with 99.5% purity. The tests were performed according to DIN 51528 and ASTM D-6743. Cleaned stainless steel pins of 1" diameter were filled with the HTF samples. Before the pins were closed the vapor spaces were filled with nitrogen at 99.9% purity. By these actions the oxygen level, the metal surface to HTF mass ratio and the contamination level were put constant in the laboratory test.

2.2. CSP plant modeling

The modeling of a heat transfer fluid system requires a matrix of data such as shown in Table 1 for example. This can be done by splitting the HTF system in sections with the same temperature. For every section the HTF mass and the time period of operation at this temperature need to be considered and the HTF degradation is determined. The degradation rate of the system is determined by the sum of degraded fluid for each section divided by the time period that is considered.

Typical industrial heat transfer systems operate with minimum temperature changes the whole year and there are just a few shut downs for maintenance and operating interruptions. The temperature distribution is simple because there is typically the target operating temperature that is generated by a heater and a second lower temperature after the consumers of the heat which is also the inlet temperature to the heater. So the system degradation can be determined by splitting the plant into 3-4 sections only.

CSP plants typically start up and shut down every day. Depending of the time of the year and the weather conditions, the maximum target temperature may not even be reached. About noon, collectors have to be defocused in order not to overheat the HTF. This makes the temperature distribution quite complex and requires multiple sections to model the CSP plant with acceptable accuracy.

A degradation model was built from laboratory test data for the DOWTHERM™ A HTF and one average low purity product. With these degradation models, the operating temperature profile of Table 1 was assumed and the theoretical degradation rate was determined.

Table 1.Temperature profile selected for CSP plant simulation

		Temperature	**Temperature**	**Wt% of total HTF system volume**
Operating hours per year	**[h]**	**2500 hours**	**6260 hours**	
		[°C]	**[°C]**	
Temperature Solar field 1/4 heating zone	hot [°C]	316.3	<293	6.5%
Temperature Solar field 2/4 heating zone	hot [°C]	339.5	<293	6.5%
Temperature Solar field 3/4 heating zone	hot [°C]	362.8	<293	6.5%
Temperature Solar field 4/4 heating zone	hot [°C]	386.0	<293	6.5%
Temperature of fluid out of the loop	hot [°C]	393.0	<293	12.5%
Temperature of fluid out of the loop	cold [°C]	300.0	<293	60.8%
Film temperature solar field 1/4 heating zone	[°C]	321.3	<293	0.2%
Film temperature solar field 2/4 heating zone	[°C]	344.5	<293	0.2%
Film temperature solar field 3/4 heating zone	[°C]	367.8	<293	0.2%
Film temperature solar field 4/4 heating zone	[°C]	398.0	<293	0.2%
				100%

Finally the model was compared with real degradation data of operating CSP plants and an adjustment was implemented. The degradation behavior for a 99.5% purity DPO/ biphenyl grade in a CSP plant was determined by applying the model.

As mentioned in section 2.1, the degradation rate also depends on the degradation concentration of the HTF. The concentration can be modified by plant operators by frequent operation of the regeneration unit (ullage system). The efficiency of degradation product separation was estimated to be 50% for high and low boiler separation. It was also assumed to send the separated degradation product blend for external regeneration with 90% HTF recovery at $1/kg regenerated fluid. The ullage system is expected to maintain the low boiler concentration at maximum 0.5% and the high boiler concentration at maximum 10% in the system. The data allows determining the required top-up demand over the life time of the CSP plant and the associated cost, which gives a cost comparison between DOWTHERM™ A HTF and the 99.5% purity grade.

2.3. Measurement of chlorine content

The chlorine content of the five commercial 99.5% purity DPO/ biphenyl grades and DOWTHERM™ A HTF was tested via combustion in combination with microcoulometric detection according to ASTM D5808.

3. Results

3.1. HTF degradation and chlorine testing

At first, the five DPO/ biphenyl HTFs with a purity level of 99.5% and DOWTHERM™ A HTF (99.9% purity) were kept in the oven at 399°C for 6 weeks. The chlorine content was also determined from the same samples. The results can be found in Table 2.

Table 2.Thermal degradation and chlorine concentration results for 5 DPO/ Biphenyl grades & DOWTHERM™ A HTF

	Degradation after 6 weeks at 399°C % degradation	Chlorine concentration ppm
DOWTHERM™ A HTF	3.3%	<0.2[1]
Grade 1 - 99.5%	6.8%	<0.2[1]
Grade 2 - 99.5%	6.8%	2.8
Grade 3 - 99.5%	8.8%	0.8
Grade 4 - 99.5%	6.2%	17.7
Grade 5 - 99.5%	7.1%	0.7

3.2. Discussion on chlorine effects

It is well documented [3] that chloride will cause pitting in steel under the right conditions. These conditions are often found under deposits, gaskets or in small crevices in a metal surface. The gasket or deposit acts as a shield producing a stagnant area that acts to concentrate any chloride present and magnifies the corrosive effect. This type of corrosion is also common in head space areas of hot systems since any water present will collect as vapor at the high points providing a favorable environment for chloride pitting corrosion. This can lead to failure of piping and relief components at the high points.

Another type of corrosion from chlorides is chloride stress corrosion cracking (CLSCC) and is most common in austenitic stainless steel such as 304 and 316. Chloride stress corrosion can occur in stainless steel at levels as low as 1-10 ppm chloride [5] and the probability increases as the chloride concentration and temperature increase. Temperature cycling is also a contributing factor. CLSCC occurs where metal is stressed such as a weld seam and a bend in tubing. CLSCC initiate from sites of localized pitting or crevice corrosion. Crack propagation occurs when the crack grows more quickly than the rate of corrosion. These cracks can lead; , to leaks at joints and ultimately weld failures all over the plant.

Since trough solar systems operate at extremely high temperatures and undergo frequent temperature cycling, it is very important that the thermal fluid not contain significant amounts of chloride. Due to their chloride level, the commercial grades 2 to 5 may not be suitable for use in parabolic trough CSP plants.

[1] Value below the detection limit of method

3.3. Extended HTF degradation testing and modeling

It was decided to extend the testing duration and temperatures with DOWTHERM™ A HTF and grade 1 which is considered to be representative for the other 4 low purity grades. The thermal degradation rate of the 99.5% purity grade is clearly higher than DOWTHERM™ A HTF. The lower the temperature the more severe the difference between 99.5% purity and DOWTHERM™ A HTF (see Fig. 1).

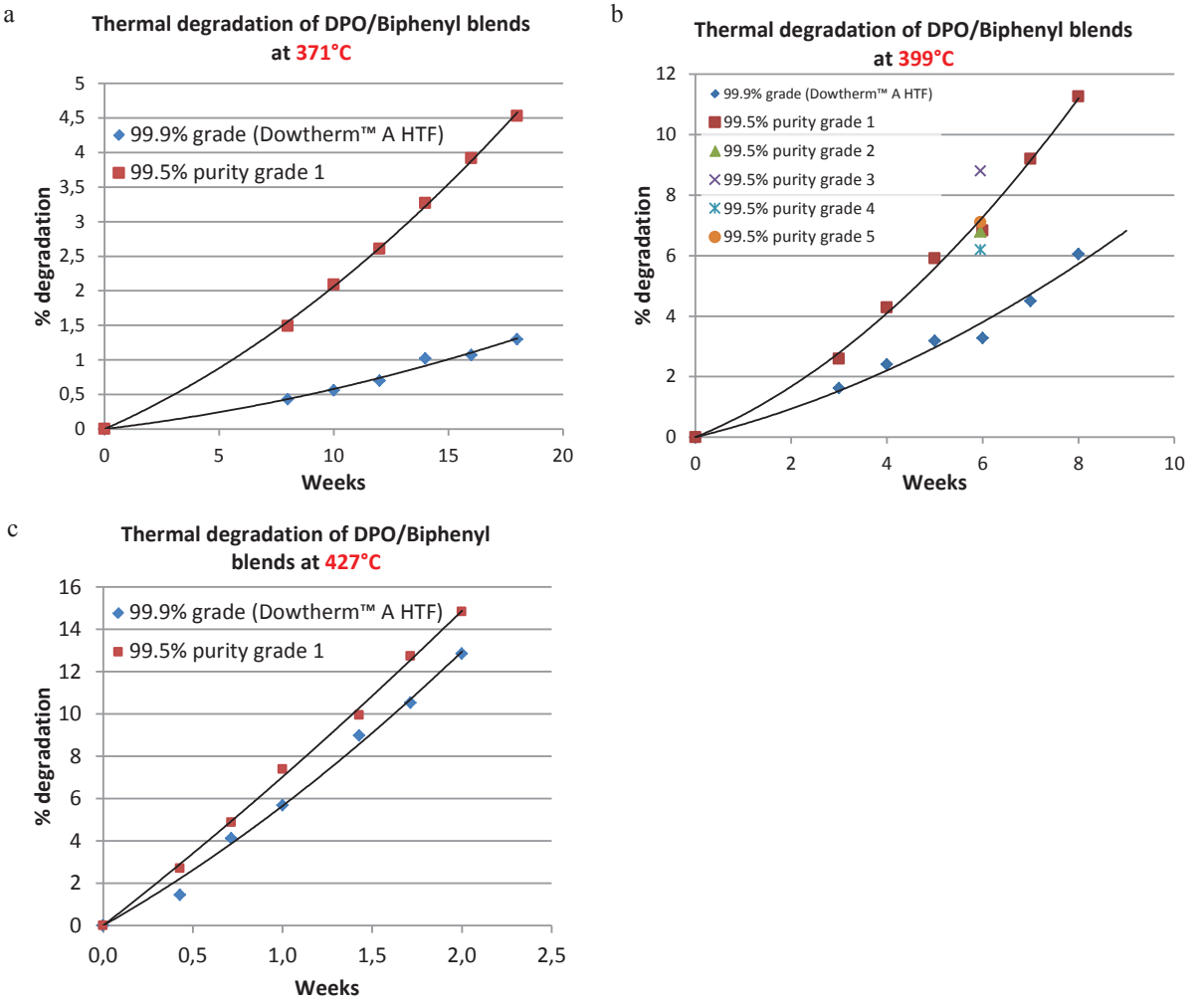

Fig. 1. Degradation rates of DPO/Biphenyl blends at different purities and 371°C (a), 399°C (b), 427°C (c).

Besides the graphs for 427°C, the graphs from Fig. 1 show increasing slopes with time which means that degradation rate increases with time. This curve shape can also be found at degradation product analysis from parabolic trough CSP plants [4]. If degraded HTF is re-purified by distillation, the degradation rate is almost reduced to the original rate. Hence, the fluid degradation depends on the concentration of degradation products as stated in section 2.1. Degradation versus time was described by an equation of second order determined by polynomial regression. Fig. 2 shows the function's derivative versus the function itself, which is equal to the degradation rate per week versus the degradation concentration in the HTF. While the degradation rate is almost the same at any degradation concentration at 427°C, the degradation rate at 371°C is more than 6 times higher for a degradation concentration of 10% compared to new HTF.

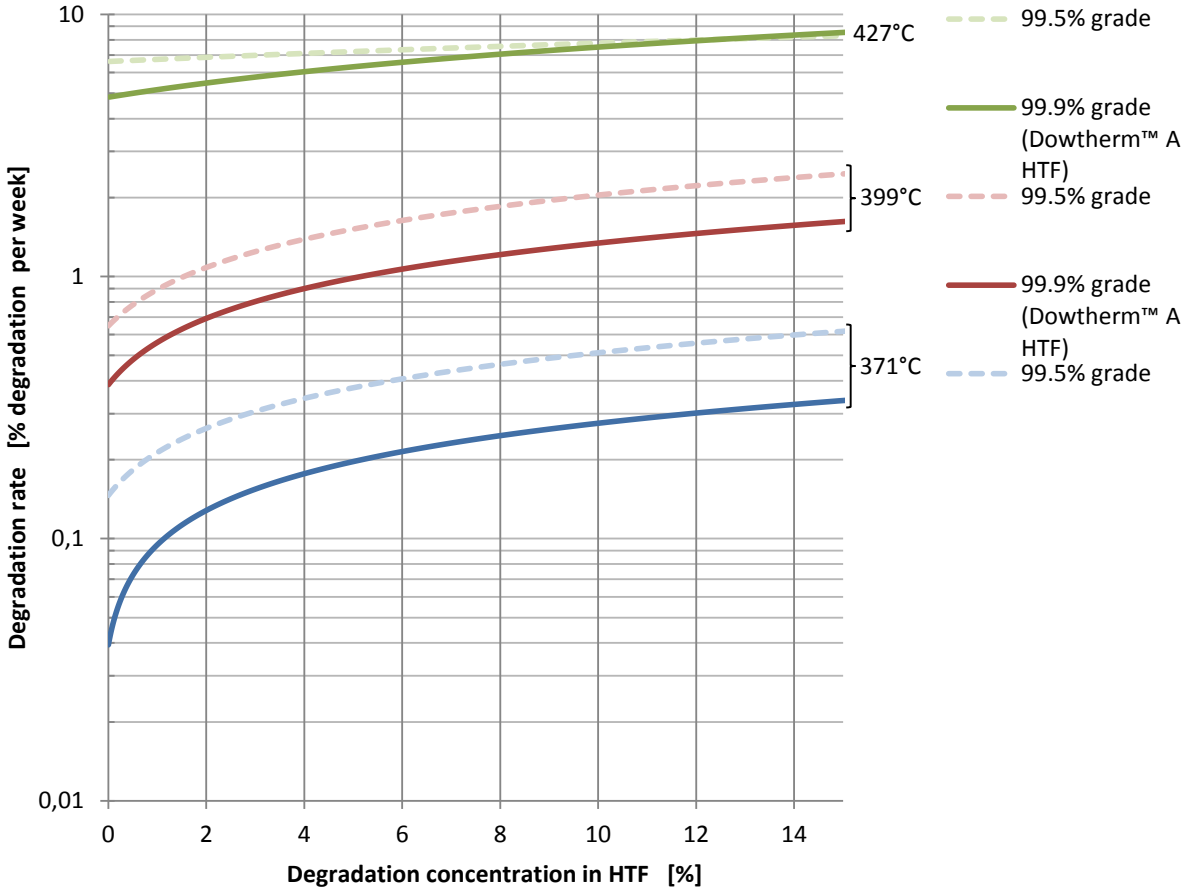

Fig. 2. Degradation rates of 99.5% DPO/Biphenyl blends & DOWTHERM™ A HTF versus degradation concentration in HTF

The current degradation rate is shown in the graph (Fig. 2) for each degradation concentration of the fluid. The degradation rate versus fluid temperature is described via the Arrhenius equation:

$$k = Ae^{-E_a/(RT)} \tag{1}$$

k degradation/ time
A factor
E_a *activation energy*
R universal gas constant
T temperature

It is known that the factor A also depends on the temperature which also applies to DPO/biphenyl degradation. The equation (2) projects the degradation rate within the relevant temperature range fairly well.

$$k = e^{(aT^2+bT+c)} \tag{2}$$

The factors *a, b, c* can be determined for any degradation concentration. As an example graphs of degradation rate versus temperature for different concentrations of DOWTHERM™ A HTF are shown in Fig. 3.

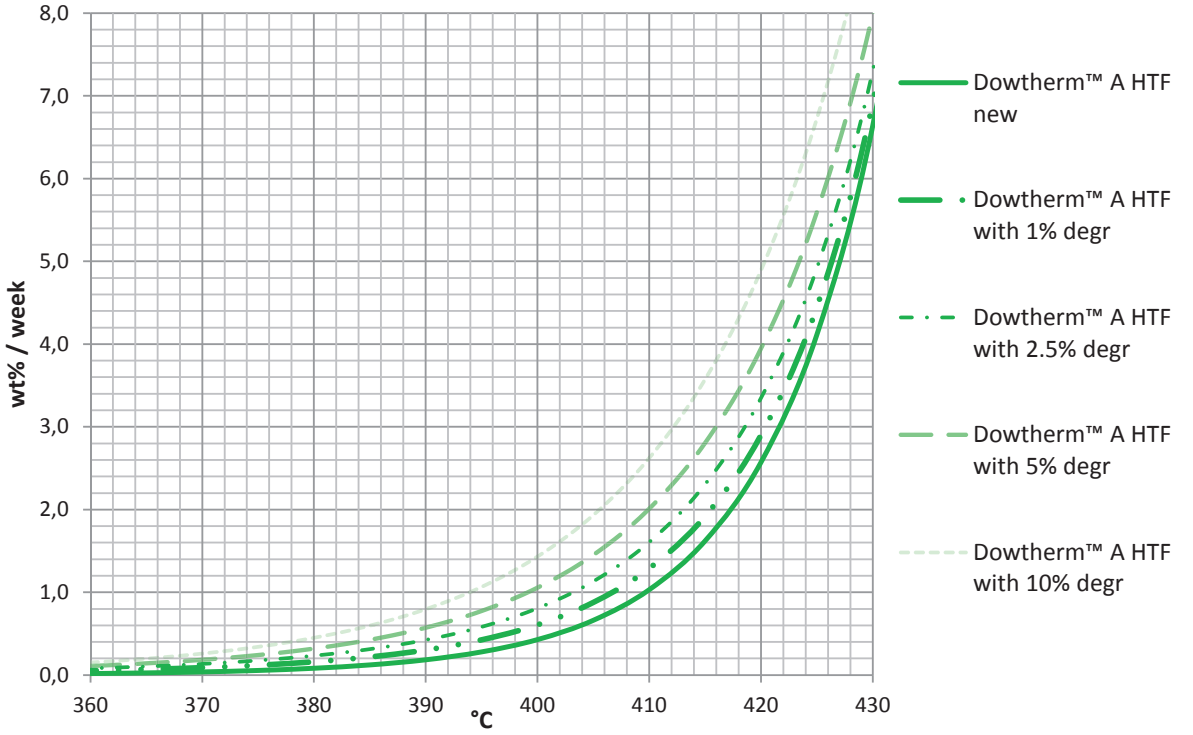

Fig. 3. Degradation rates of DOWTHERM™ A HTF versus temperature for different degradation concentrations

3.4. Modeling of HTF degradation in a CSP plant

Applying the model to the temperature profile of the CSP plant example (Table 1), fluid degradation concentration in a CSP plant over time can be determined. The model was also adjusted to DOWTHERM™ A HTF degradation data from CSP plants, which is applied in the graph of (Fig. 4a). The 99.5% grade would form 1.7-2.4 times more degradation products for the same operating time. The graph of Fig. 4a considers neither any fluid exchange nor the operation of the ullage system.

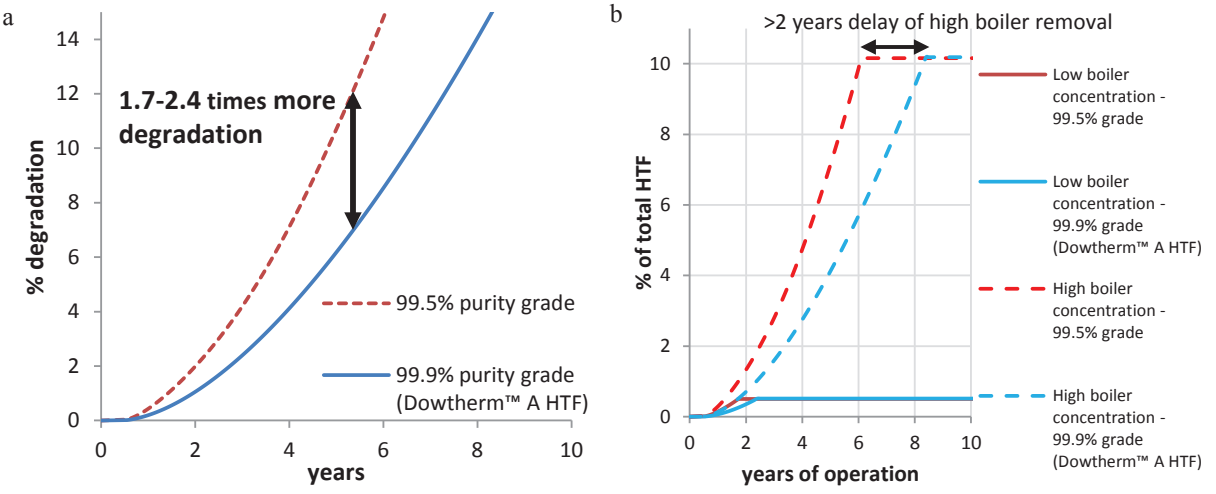

Fig. 4. Degradation concentration in a trough CSP plant over time a: no degradation removal; b: control high and low boilers at 10% / 0.5%

If the ullage system is operated like in section 2.2, low and high boiler concentration in the HTF of the CSP plant behaves as shown in Fig. 4b. Taking a maximum of 10% high boiler content as a target, the ullage system needs to start separating high boilers after about 6 years of CSP plant operation for the 99.5% grade whilst this can be delayed to 8 years with DOWTHERM™ A HTF, before high boilers need to be separated. If the assumptions of section 2.2 on ullage system operation are applied for a CSP plant operation period of 25 years, over 30% more top up demand is required if the 99.5% grade was initially filled to the system instead of a high quality grade with 99.9% purity (Fig. 5a). In regards of cost an additional US$ 2 per kg initially filled fluid needs to be spent during 25 years of plant operation (Fig. 5b) including the cost for new HTF and the external regeneration of separated HTF degradation product mix.

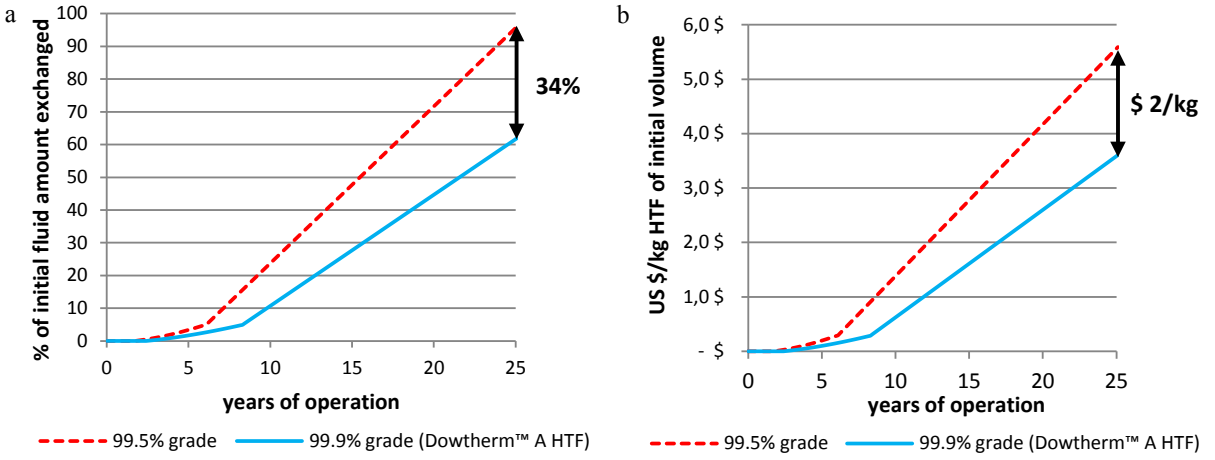

Fig. 5. HTF top up demand (a) and cost (b) for 25 years of CSP plant operation for DOWTHERM™ A HTF and the 99.5% grade

3.5. Discussion of modeling results

3.5.1. Degradation model versus temperature

The model was performed based on 3 temperature points which covers the relevant degradation temperature range. Degradation rates outside the range may result in wrong conclusions. Results between 350°C and 430°C can be considered to be exact enough for CSP degradation estimates.

3.5.2. High and low boiler composition of HTF

In the model used for top up demand calculation, the low boiler – high boiler ratio is 0.5% to 10% which deviates from the natural ratio of 1/3 low boilers and 2/3 high boilers. Laboratory tests [1] have shown this ratio keeps stable if no degradation products are separated during the heating time. The modification of the ratio by ullage system operation may impact the degradation rate which has not been considered by the model of this work. Furthermore the ullage system may not separate all components of degradation products equally well. For example very heavy high boiling products such as Diphenoxybiphenyl separate better from DPO/biphenyl than lighter high boilers such as o-terphenyl. The resulting change of degradation composition may also influence the degradation build up in operational plants which this model does also not consider.

3.5.3. Temperature profile of CSP plants

The temperature profile used in this model is applicable for a CSP plant without energy storage with high direct normal irradiance (DNI) over 2500 kWh/m²/y. The degradation rate at locations with lower DNI can be significantly smaller. The plant capacity factor may also impact degradation rate as well as the piping design. The reduction of the hot piping volume brings a significant reduction in degradation rate for example.

4. Conclusions

A well designed HTF ullage system is important to maintain degradation concentration at low levels and keep the degradation rate and the top up cost low.

Low purity DPO/Biphenyl based fluids might initially be at lower cost, but result in higher degradation over the fluid life time resulting in higher cost for the fluid life time of the plant.

Grades with chloride and sulfur levels in the ppm range may not be suitable for use in CSP plants due to the risk of leaks and expensive equipment replacements from stress corrosion cracking.

5. Perspective

The authors are aware that many assumptions have been made to come to the final results of top up cost differences and differences to these results are possible. The magnitude of the results is correct and allows conclusions of significant higher cost for the use of a 99.5% grade of HTF. The developed models can be improved with continued tracking of operating and degradation data and will allow more precise predictions in the future.

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